

AD 740829

Technical Progress Report 72-1 Semiannual
September 1, 1971 to February 29, 1972

SENSITIVITY FUNDAMENTALS

By: P. S. DeCARLI, D. S. HOSS, R. SHAW, and R. W. WOOLFOLK

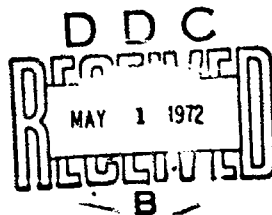
Prepared for:

OFFICE OF NAVAL RESEARCH
DEPARTMENT OF THE NAVY
ARLINGTON, VIRGINIA

CONTRACT N00014-70-C-0190

Reproduction in whole or in part is permitted for any purpose of the United States Government

Prior Report
AD 731416



Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151



STANFORD RESEARCH INSTITUTE
Menlo Park, California 94025 · U.S.A.

DISTRIBUTION STATEMENT A
Approved for public release
Distribution Unlimited

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

Security classification of title, body of abstract and indexing, and data in this report is shown in the overall report classification.

1. ORIGINATING ACTIVITY (Corporate author) Stanford Research Institute 333 Ravenswood Avenue Menlo Park, California		20. REPORT CLASSIFICATION UNCLASSIFIED	
3. REPORT TITLE SENSITIVITY FUNDAMENTALS			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Progress Report 72-1 September 1, 1971 to February 29, 1972			
5. AUTHOR(S) (First name, middle initial, last name) David S. Ross, Robert Shaw, Robert W. Woolfolk, Paul S. De Carli			
6. REPORT DATE April 1972		7a. TOTAL NO. OF PAGES 66	
		7b. NO. OF PAGES 17	
8a. CONTRACT OR GRANT NO. N00014-70-C-0190		9. ORIGINATOR'S REPORT NUMBER(S) Technical Progress Report 72-1 Semiannual	
8b. PROJECT NO. SRI Project PRU 8525			
8c. SRI SRI		10. OTHER REPORTS (Any other numbers that may be assigned this report)	
11. ABSTRACT STATEMENT Reproduction in whole or in part is permitted for any purposes of the United States Government.			
12. SUPPLEMENTARY NOTES None		13. DISTRIBUTION STATEMENT Office of Naval Research Department of the Navy Arlington, Virginia	
14. SUMMARY <p>This report summarizes a six-month period of research on the relationship between detonation phenomena, chemical structure, and kinetics for isomeric dinitropropanes and other nitroalkanes, sponsored by the Office of Naval Research. Research on dinitropropanes is being carried out in three areas: high velocity detonation (HVD), low velocity detonation (LVD), and static high pressure and kinetic effects.</p> <p>Shock pressures for 1-sec reaction time were 89 and 100 kbars respectively for 1,1-DNE and 1,1-DNP. An α-hydrogen effect on reaction times was found for 1,1-DNP and 2,2-DNP at 60°; and 1,1-DNE and 1,1,1-FDNP at 25°. The isomers methyl nitrite and nitromethane have similar reaction times at shock pressures of 57 and 79 kbar respectively. The constant, u_3, for a Universal Hugoniot has been evaluated as ~ 2 by several procedures.</p> <p>There is a qualitative relationship between LVD sensitivity and the ratio, H_F/H_D, but other factors also must play a role since dinitroalkanes with similar ratios have very different LVD sensitivities.</p> <p>Reaction time measurements at 10 kbar for several dinitroalkanes give a shorter time for 1,1-DNP than for 2,2-DNP or 1,1,1-FDNP with a marked change in reaction time with temperature for 1,1,1-FDNP.</p> <p>Products studies for VLPP at four dinitroalkanes show that 1,2-DNP decomposes by a 5-center mechanism while 1,1-, and 2,2-DNP and 1,1,1-FDNP all decompose via C-N scission, results consistent with kinetic parameters measured earlier.</p>			

DD FORM 1473 (PAGE 1)

54

5/A G1G1-807-4601

Security Classification

UNCLASSIFIED

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
sensitivity fundamentals						
liquid explosives						
gap sensitivity						
detonation phenomena						
decomposition kinetics						
low velocity detonation						
high velocity detonation						
TIGER code						
very low pressure pyrolysis						
high pressure decomposition						
kinetics of decomposition						
Arrhenius parameters						
activation energies						
explosion reaction times						
shock temperatures						
sensitivity testing						
1,1-dinitropropane						
2,2-dinitropropane						
1,2-dinitropropane						
1,1,1-fluorodinitropropane						
1,1-dinitroethane						
nitromethane						
methyl nitrite						
1,2-difluoraminopropane						
2,2-difluoraminopropane						



STANFORD RESEARCH INSTITUTE
Menlo Park, California, 94025 : U.S.A.

*Technical Progress Report 72-1 - Semiannual
September 1, 1971 to February 29, 1972*

April 1972

SENSITIVITY FUNDAMENTALS

By: P. S. DeCARLI, D. S. ROSS, R. SHAW, and R. W. WOOLFOLK

Prepared for:

OFFICE OF NAVAL RESEARCH
DEPARTMENT OF THE NAVY
ARLINGTON, VIRGINIA

CONTRACT N00014-70-C-0180

SRI Project PRU 8626

Reproduction in whole or in part is permitted for any purpose of the United States Government.

Approved by:

M. S. HILL, Director
Physical Sciences (Chemistry)

CHARLES J. COOK, Executive Director
Physical Sciences Division

PREFACE

This project is the responsibility of the Chemistry Laboratory's Physical Organic Chemistry Group in the Physical Sciences Division of Stanford Research Institute. Project organization and principal contributors to the technical work are:

Program Manager:	M. E. Hill
Project Supervisor:	T. Mill
Low-Velocity Detonation:	R. W. Woolfolk
Physics and Chemistry of Detonation:	R. Shaw
Static High-Pressure and Kinetic Effects:	D. S. Ross L. W. Piszkwicz P. S. De Carli R. Shaw

SUMMARY

Physics and Chemistry of Detonation

The high-speed streak camera has been moved successfully from Calaveras to Corral Hollow Experimental Site (CHES). A calibration shot at CHES with nitromethane gave results similar to previous shots at Calaveras. The smooth-shock reaction time for liquid methyl nitrite at 10 atm with a preshock temperature of 25°C was found to be 1.15 μ sec for a shock pressure of 57 kbar, about 26 kbar less than for the same reaction time of isomeric nitromethane. This is the biggest difference in shock pressure (at constant reaction time) measured for two isomers and is attributed to the 17 kcal/mole difference in bond dissociation energies of the weak bonds of the two isomers.

Interesting differences in shock initiation were found for dinitroalkanes. The shock pressure required to give a 1 μ sec reaction time was about 89 kbar for 1,1-DNE and 100 kbar for 1,1-DNP. We also found an α -hydrogen effect on shock initiation. At a preshock temperature of 60°C, the reaction time of 1,1-DNP was 2.2 μ sec at 91 kbar, whereas the reaction time of 2,2-DNP was greater than 4 μ sec (failed to detonate) at 98 kbar. At a preshock temperature of 25°C, the reaction time of 1,1-DNE was 0.8 μ sec at 90 kbar, whereas the reaction time of 1,1,1-FDNE was greater than 4 μ sec (failed to detonate) at 96 kbar. In both these comparisons, namely, 1,1-DNP versus 2,2-DNP, and 1,1-DNE versus 1,1,1-FDNE, the compound with no α -hydrogen was less reactive than the compound that had a hydrogen atom α to the dinitro group.

We have recorded detonation failure waves of 1,1-DNP using the previously developed brass cone technique. The gross features of the imprints are similar to those observed for IBA.

We previously discussed a "universal" Hugoniot for liquids, that had the form,

$$U_s/c_0 = 1.37 - 0.37 \exp [-u_3 u_p / c_0] + 1.62 u_p / c_0$$

where U_s is the shock velocity, u_p is the particle velocity, c_0 is the sonic velocity, and u_3 is a constant. The value of u_3 is thermodynamically related to the variation in the speed of sound and the variation of specific volume with pressure close to atmospheric pressure. We have used data from echo-sounding tables for pure water, together with p-v-T data, to evaluate the necessary derivatives graphically, and obtained a value for $u_3 \sim 2$. Some shock wave data on glycerin obtained by Dr. D. Erlich of SRI on another project suggest that $u_3 = 1$ to 2. We suggest that a value of $u_3 = 2$ is consistent with both sets of data.

Low-Velocity Detonation

TIGER equilibrium calculations were made on the difluoraminoalkanes and were compared with values for dinitroalkanes that were previously reported. The comparisons show that the energy release of those systems containing C-H-O were greatly dependent on the temperature and pressure, while the systems containing fluorine showed little variation. This is due primarily to the stability of HF in relation to other fluorine containing compounds.

The correlation between the low-velocity detonation (LVD) gap sensitivity and the ratio of the heat of reaction to heat of vaporization, $\Delta H_r / \Delta H_v$, gives a qualitative ordering of the compounds so far tested.

This correlation does not differentiate between the dinitroalkanes. Therefore, factors other than kinetics and heat of vaporization must be important to the LVD behavior of the dinitroalkanes.

Experiments for measuring the pressure field in an LVD liquid as a function of time have been started. This technique uses manganin gages to record the pressure in the 0-20 kbar range. We hope this technique will enable us to relate the energy in the liquid and in the container walls to LVD propagation.

Static High Pressure and Kinetic Effects

Static high-pressure (SHP) experiments at 10 kbar on several dinitroalkanes with and without α -hydrogens show that, as in reaction time measurements, a compound with an α -hydrogen (1,1-DNP) is more reactive than those compounds without (1,1,1-FDNP and 2,2-DNP). The reason for the shorter explosion time for 1,1-DNP is not clear. 1,1,1-FDNP shows a very sharp increase in explosion time on going from 245° to 228°C, similar to that found for nitromethane (NM) at 1 kbar.

Studies of the very low-pressure pyrolysis (VLPP) of dinitropropanes are completed, and the products of these decompositions indicate that there are two processes. For the nongeminate dinitroalkane, 1,2-DNP, the sole products isolated are the nitroolefins, 1- and 2-nitropropene. Thus this compound behaves like a simple nitroalkane and undergoes five-center elimination of HONO. The gem-dinitroalkanes, on the other hand, 1,1,1-FDNP, 1,1- and 2,2-DNP, undergo initial C-N scission, followed by migration of oxygen from nitrogen to carbon to give propionyl fluoride, propionaldehyde, and acetone, respectively. β -scission competes with O-migration in the cases of 1,1- and 2,2-DNP.

CONTENTS

PREFACE	ii
SUMMARY	iii
LIST OF ILLUSTRATIONS	viii
LIST OF TABLES	x
GLOSSARY OF COMPOUNDS	xi
I INTRODUCTION	1
A. Physics and Chemistry of Detonation	1
B. Low-Velocity Detonation	2
C. Static High-Pressure and Kinetic Effects	2
II PHYSICS AND CHEMISTRY OF DETONATION	3
A. Introduction	3
B. Measurement of Smooth-Shock Reaction Times	3
C. Detonation Failure	10
D. "Universal" Hugoniot for Liquids	18
E. Publications	25
F. Future Work	27
G. Acknowledgments	27
III LOW-VELOCITY DETONATION	28
A. Introduction	28
B. TIGER Calculations	29
C. Experimental Work	40
D. Pressure-Time Studies	40
E. Future Work	42

IV	STATIC HIGH-PRESSURE AND KINETIC EFFECTS	43
A.	Introduction	43
B.	Static High-Pressure Experiments	43
C.	VLPP of Nitroalkanes	47
D.	Future Work	50
REFERENCES	52
DOCUMENT CONTROL DATA FORM DDL473	54

ILLUSTRATIONS

Figure 1	Smooth-Shock Reaction Time Measurements for Nitromethane and Methyl Nitrite at a Preshock Temperature of 25°C . . .	4
Figure 2	Smooth-Shock Reaction Time Measurements for Nitromethane and Methyl Nitrite at Preshock Temperatures of -25°C and -50°C	7
Figure 3	Cell for Reaction Time Measurements for Methyl Nitrite at 10 Atmospheres Preshock Pressure and 25°C Preshock. . .	9
Figure 4	Smooth-Shock Reaction Time Measurements for 1,1-DNE and 1,1-DNP at a Preshock Temperature of 25°C	11
Figure 5	Smooth-Shock Reaction Time Measurements for 1,1-DNP and 2,2-DNP at a Preshock Temperature of 60°C	12
Figure 6	Smooth-Shock Reaction Time Measurements for 1,1-DNE and 1,1,1-FDNE at a Preshock Temperature of 25°C	13
Figure 7	Effect of Preshock Temperature on Smooth-Shock Reaction Time Measurements for Methyl Nitrite	14
Figure 8	Effect of Preshock Temperature of Smooth-Shock Reaction Time Measurements for 1,1-DNP	15
Figure 9	Brass Cone and Cylinder Before Firing (one-half actual size)	16
Figure 10	Failure Waves Embossed on Brass Cone by Detonation in IBA. The cone is rotated slightly in successive pictures . . .	17
Figure 11	Failure Waves Embossed on Two Sides of Brass Cone After Detonation of 1,1-DNP	19
Figure 12	Failure Waves Embossed on Two Halves of Brass Cylinder After Detonation of 1,1-DNP	20

ILLUSTRATIONS (concluded)

Figure 13	Normalized $U_s - u_p$ Plot	21
Figure 14	Sound Speed in Pure Water as a Function of Specific Volume at Pressures of 1, 50, 100, and 100 bar	24
Figure 15	Calculated Normalized $U_s - u_p$ Plots for Values of $u_3 = 0.1, 1, 2, 5, 10$, and ∞ , and Showing Erlich's Experimental Glycerin Data.	26
Figure 16	Mole Percent as a Function of Temperature for 1,2-DP (TIGER)	30
Figure 17	Mole Percent as a Function of Temperature for 1BA (TIGER)	31
Figure 18	Mole Percent as a Function of Temperature for 1,1-DNE (TIGER)	32
Figure 19	Mole Percent as a Function of Temperature for 1,1-DNP (TIGER)	33
Figure 20	Mole Percent as a Function of Temperature for 1,1,1- FDNP (TIGER)	34
Figure 21	Mole Percent as a Function of Temperature for 1BA at 10 kbar (TIGER)	35
Figure 22	Mole Percent as a Function of Temperature for 1,1-DNE at 10 kbar (TIGER)	36
Figure 23	Typical Pressure-Time History for Shocked LVD Liquid	41
Figure 24	Thermal Explosion Times as a Function of Temperature for some Dinitroalkanes at 10 kbar	44

TABLES

I	Smooth-Shock Reaction Times for Nitroalkanes	5
II	Comparison of Properties of Methyl Nitrite and Nitromethane .	6
III	Calculated Energy Release for Selected Compounds at 20 kbar .	38
IV	LVD Gap Sensitivities and $\Delta H_f / \Delta H_v$ at 2000°K and 20 kbar for Selected Compounds	39
V	Thermal Explosion Times of Dinitroalkanes at Static High Pressures	45
VI	VIPP Products from Dinitropropanes	48

GLOSSARY OF COMPOUNDS

<u>Code Name</u>		<u>Chemical Name</u>
1,1-DNP	$\text{CH}_3\text{CH}_2\text{CH}(\text{NO}_2)_2$	1,1-dinitropropane
2,2-DNP	$\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_3$	2,2-dinitropropane
1,2-DNP	$\text{CH}_3\text{CH}(\text{NO}_2)\text{CH}_2\text{NO}_2$	1,2-dinitropropane
1,1-DNE	$\text{CH}_3\text{CH}(\text{NO}_2)_2$	1,1-dinitroethane
EN	$\text{CH}_3\text{CH}_2\text{ONO}_2$	ethyl nitrate
1,1,1-FDNE	$\text{FC}(\text{NO}_2)_3\text{CH}_3$	1,1,1-fluorodinitroethane
1,1,1-FDNP	$\text{FC}(\text{NO}_2)_2\text{CH}_2\text{CH}_3$	1,1,1-fluorodinitropropane
1,2-DP	$\text{CH}_3\text{CH}(\text{NF}_2)\text{CH}_2\text{NF}_2$	1,2-bis(difluoramino)propane
2,2-DP	$\text{CH}_3\text{C}(\text{NF}_2)_2\text{CH}_3$	2,2-bis(difluoramino)propane
IBA	$(\text{CH}_3)_2\text{C}(\text{NF}_2)\text{CH}_2\text{NF}_2$	1,2-bis(difluoramino)-2-methylpropane
1,2-DB	$\text{CH}_3\text{CH}_2\text{CH}(\text{NF}_2)\text{CH}_2\text{NF}_2$	1,2-bis(difluoramino)butane
NM	CH_3NO_2	nitromethane

I INTRODUCTION

Under the sponsorship of the Office of Naval Research (ONR), Stanford Research Institute is studying the fundamental sensitivity properties of liquid high-energy materials in order to define the minimum number of physical and chemical parameters of the system needed to predict detonation sensitivity. In this work we have been concerned primarily with: (1) detonability of the liquid phase, i.e., whether it will support a detonation wave, and the failure diameter for detonation; (2) the necessary conditions for initiating detonation and whether ease of initiation is related to structure; and (3) the mode of decomposition of the chemical structure and the relationship of the initial decomposition steps with the phenomena of (1) and (2).

In previous work on this contract,* these relationships were studied with isomeric difluoraminopropanes and butanes, and we are now studying nitro compounds in the analogous isomeric propane series and some ethane homologs. Thus a direct comparison between the two high-energy groups that are of most interest at present can be made, and basic knowledge can be obtained on the initiation and propagation properties of model liquid nitroaliphatic plasticizers.

This program consists of three primary tasks;

A. Physics and Chemistry of Detonation

The ultimate objective of studies of the physics and chemistry of detonation (Section II) is to correlate transient detonation phenomena, such as shock initiation and failure behavior, with the mode of decom-

* Stanford Research Institute Project 4051, Final Report, "Sensitivity Fundamentals," May 15, 1970.

position. This objective involves: (1) measurement of failure diameters, (2) study of events in the liquids as shocks of various magnitudes enter, and (3) measurement, evaluation, and correlation of physical and thermochemical properties.

B. Low-Velocity Detonation

The objectives of this program (Section III) are to determine under which conditions LVD will initiate and to relate this initiation to the chemical and physical properties of the materials. By comparing two classes of materials (i.e., the difluoramino and dinitro compounds) with such widely different thermochemical and kinetic properties, we can ascertain those factors that influence LVD initiation.

C. Static High-Pressure and Kinetic Effects

Section IV of this research effort comprises a study of the decomposition behavior of shock-sensitive liquids at very low and very high pressures including measurements of reaction times at pressures and temperatures comparable to those encountered in initiating shocks; and attempts to describe a relationship between detonation phenomena and chemical mechanism, including the elementary rate steps.

II PHYSICS AND CHEMISTRY OF DETONATION

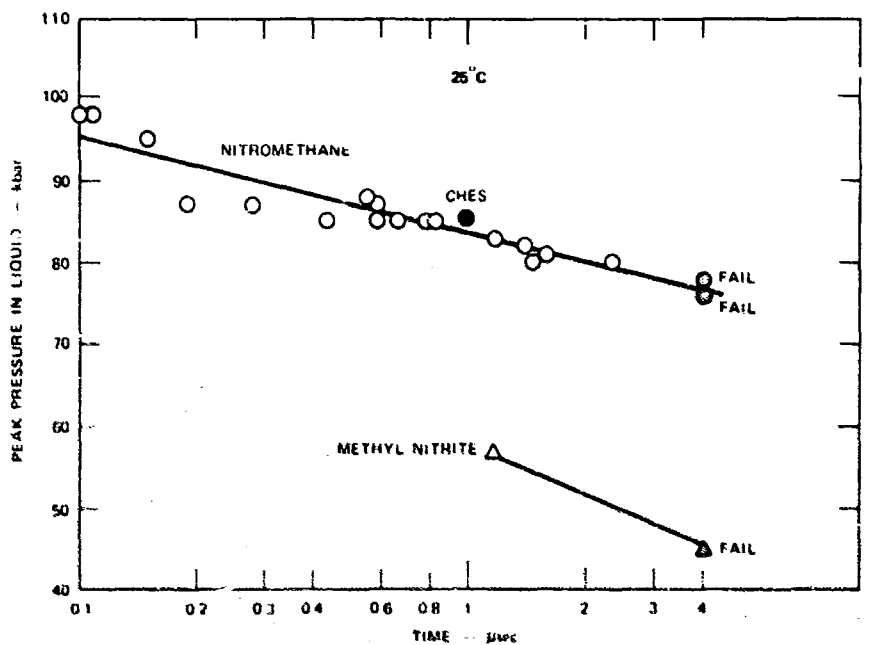
(Robert Shaw)

A. Introduction

The objective of this part of the research program is to improve the understanding of the physical and chemical processes that occur in two transient detonation phenomena, namely, shock initiation and detonation failure. We have used a three-fold approach: (1) experimental observation of the phenomenon itself (for example, smooth-shock reaction time measurements for shock initiation, and brass imprints for detonation failure), (2) testing of models (homogeneous thermal explosion theory for shock initiation, and Drenin's theory for detonation failure), and (3) obtaining input data for the models, such as calculated shock temperatures, and kinetics of heat-releasing chemical reactions at known temperatures and pressures as close as possible to detonation conditions. During the present report period we have obtained some interesting results on items (1) and (3) and plan to devote a major part of the next period to item (2).

B. Measurement of Smooth-Shock Reaction Times

The high-speed camera was moved successfully from Calaveras to Corral Hollow Experiment Site (CHES). A test shot at CHES with nitromethane (NM) at a preshock temperature of 25°C gave a smooth-shock reaction time of 0.98 μ sec at a shock pressure of 85 kbar, compared with a shock reaction time of 0.78 μ sec predicted by previous shots at Calaveras (see Figure 1).



TA 8525 51

FIGURE 1 SMOOTH-SHOCK REACTION TIME MEASUREMENTS FOR NITROMETHANE AND METHYL NITRITE AT A PRESOCK TEMPERATURE OF 25°C

The results of smooth-shock reaction time measurements obtained at CHES during the last report period are given in Table I.

Table I

SMOOTH-SHOCK REACTION TIMES FOR NITROALKANES^a

Compound	Preshock Temperature (°C)	Peak Pressure in Attenuator (kbar)	Peak Pressure in Liquid (kbar)	Reaction Time (μsec)
Nitromethane	24	104	85	0.98
Methyl nitrite	25	72	57	1.16
1,1-DNP	25	109	99	1.61
1,1-DNP	26	104	95	Failed (>4)
1,1-DNP	60	100	91	2.15
2,2-DNP	60	107	98	Failed (>4)
1,1,1-FDNE	25	99	89	Failed (>4)
1,1,1-FDNE	25	107	97	Failed (>4)

^a Measured at CHES.

One of the basic ideas in this program is to use isomers that have similar physical properties so that differences in behavior can be attributed to differences in chemical structure. Nitromethane has no geometrical isomer, but one of its structural isomers is methyl nitrite, CH_3ONO . The properties of methyl nitrite are compared with those of nitromethane in Table II.

Table II

COMPARISON OF PROPERTIES OF METHYL NITRITE AND NITROMETHANE

Compounds	Methyl Nitrite	Nitromethane	Ref.
Structural Formula	CH_3ONO	CH_3NO_2	
Arrhenius parameters for gas-phase Thermal Decomposition:			
A-factor/(sec^{-1})	10^{16}	$10^{15.6}$	1
Activation energy/(kcal/mole)	42	59	1
Gas-phase thermodynamic properties:			
$\Delta H_f^\circ(298)$ /(kcal/mole)	-15.6	-17.9	1
$S^\circ(298)$ /(cal/(mole-deg))	72.3	65.8	1
$C_p^\circ(298)$ /(cal/(mole-deg))	15.4	16.8	1
Heat of vaporization/(kcal/mole)	5	9.2	2,3
Heat of formation of liquid/(kcal/mole)	-20.6	-27.1	
Boiling point/(°C)	-12	101	4
Melting point/(°C)	-17	-29	4

The compounds have similar thermodynamic properties, but the kinetics of decomposition are very different because of differences in bond strength, $D(\text{CH}_3\text{O}-\text{NO}) \sim 40$ kcal/mole and $D(\text{CH}_3-\text{NO}_2) \sim 60$ kcal/mole. The only problem with methyl nitrite is its volatility. In previous work,⁵ this was overcome by working at very low temperatures (see Figure 2). However, this approach led to other problems such as the possibility of freezing the methyl nitrite, and it made difficult a comparison with ambient temperature results. Therefore, we used the alternative approach of working at higher pressures. The vapor pressure of methyl nitrite at 25°C is

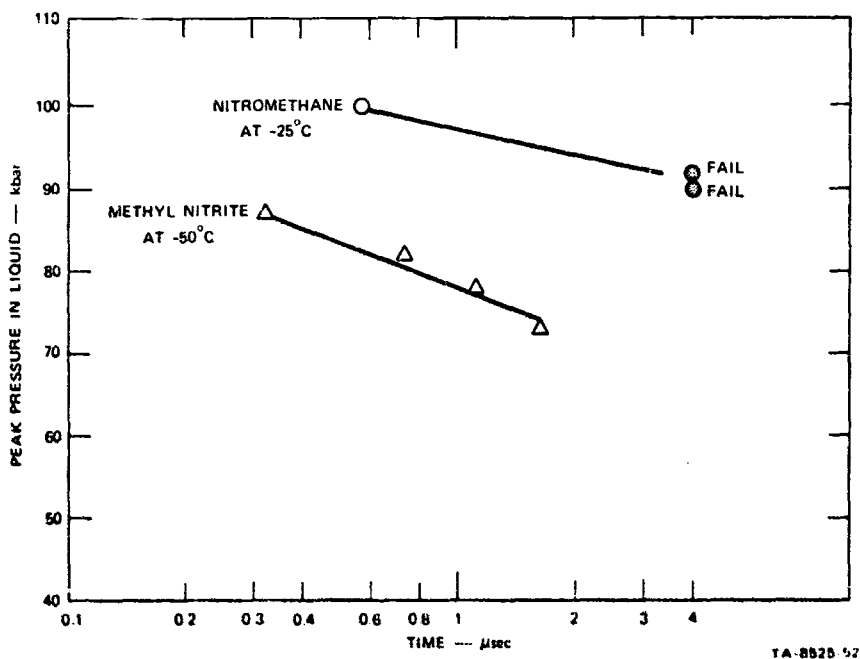


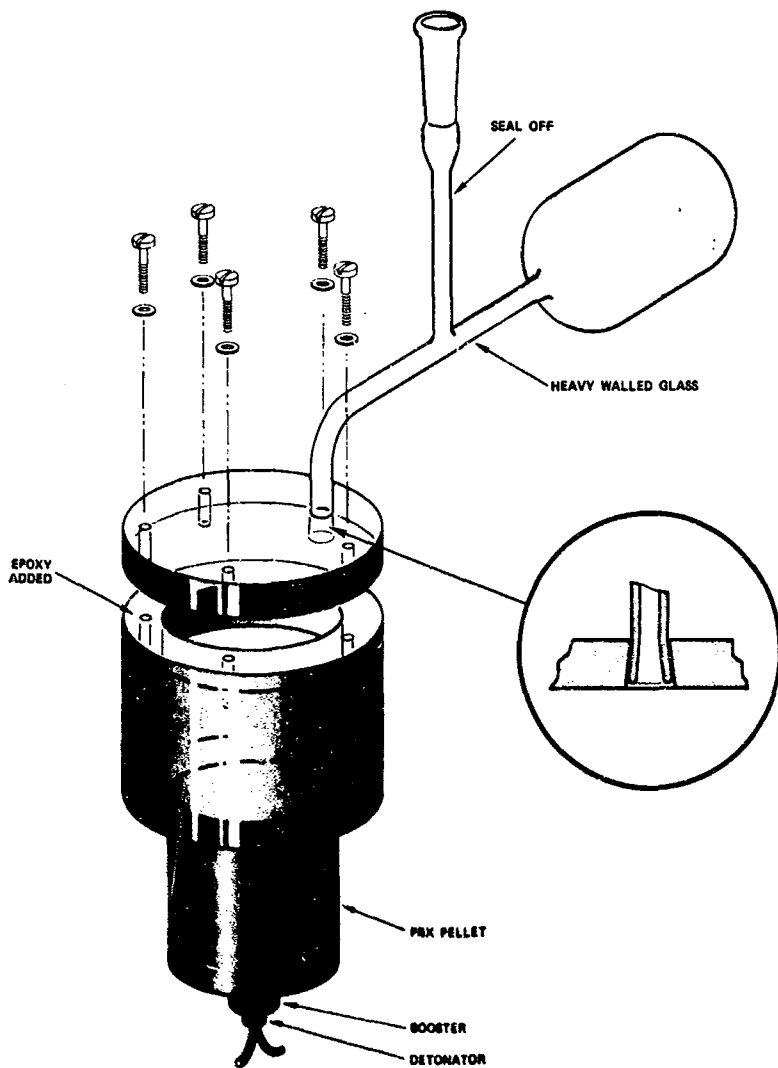
FIGURE 2 SMOOTH-SHOCK REACTION TIME MEASUREMENTS FOR NITROMETHANE AND METHYL NITRITE AT PRESOCK TEMPERATURES OF -25°C AND -50°C

about 10 atmospheres. This is still negligible compared with shock pressure and is reasonable for making a reaction cell assembly. The experimental arrangement is shown in Figure 3 and was described in the last report⁶ on this contract.

It should be pointed out that the geometry of the shots is such that quenching rarefactions destroy the initiating pressure wave after about 3 to 4 μ sec. A "failure" therefore places a minimum reaction time of, say, 4 μ sec at that pressure and places a limit on the position of the reaction time/pressure plot in that region. In several of the dinitroalkanes experiments for which we are still gathering data, some of the slopes of the reaction time/pressure plots have been sketched in (dotted lines) on the basis of our previous experience with the general shape of reaction time/pressure plots.

In a previous experiment⁶, when the attenuator thickness corresponded to a peak shock pressure of 45 kbar in the liquid methyl nitrite, there was no initiation, giving the lower limit in Figure 1. In an experiment recently completed using the high-pressure (10 atmospheres) reaction cell⁴, the smooth-shock reaction time for liquid methyl nitrite at a pre-shock temperature of 25°C was found to be 1.15 μ sec for a shock pressure of 57 kbar (Figure 1), that is about 26 kbar less than for the same reaction time of the isomer nitromethane. This is the biggest difference in shock pressure (at constant reaction time) measured for two isomers and is attributed to the large difference in bond dissociation energies of 17 kcal/mole (Table II). The experiments on methyl nitrite are now completed.

In the dinitroalkane series, some interesting differences in shock initiation have become apparent. Comparing 1,1-dinitroethane (1,1-DNE) and 1,1-DNP, which differ by only a methylene group, the shock pressure required to give a 1- μ sec reaction time is about 89 kbar for 1,1-DNE and



TC-6829-40

FIGURE 3 CELL FOR REACTION TIME MEASUREMENTS FOR METHYL NITRITE AT 10 ATMOSPHERES PRESOCK PRESSURE AND 25°C PRESOCK TEMPERATURE

100 kbar for 1,1-DNP (see Figure 4). This difference in shock reactivity is in line with intuitive expectations,^{*} but is in contrast to the difluoroaminoalkane series where 1,2-bis(difluoramino)propane (1,2-DP) and 1,2-bis(difluoramino)butane (1,2-DB) were almost identical.⁶

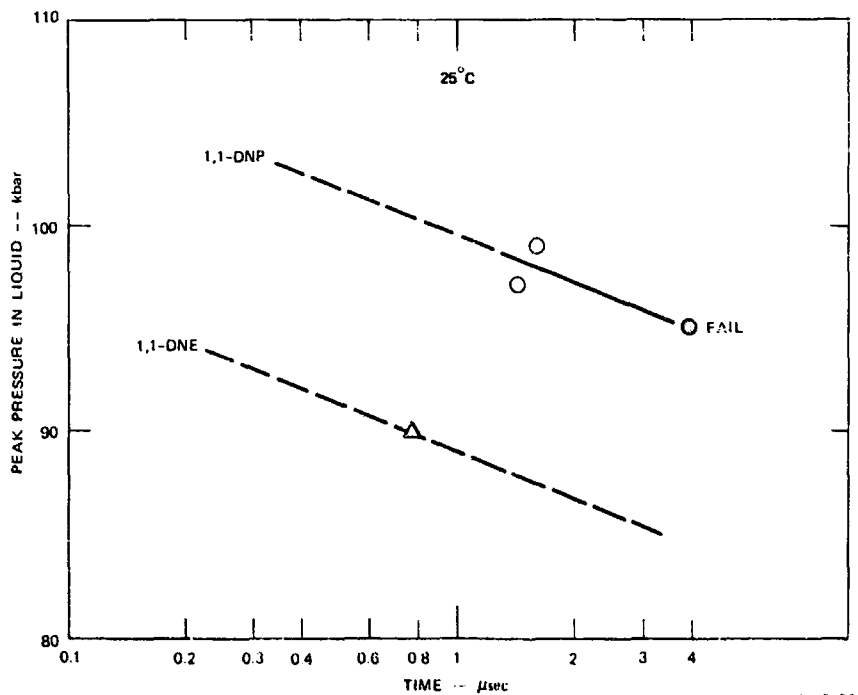
Another interesting correlation is the so-called α -hydrogen effect. At a preshock temperature of 60°C, the reaction time of 1,1-DNP was 2.2 μ sec at 91 kbar, where the reaction time of 2,2-DNP was greater than 4 μ sec (failed to detonate) at 98 kbar (see Figure 5). Similarly, at a preshock temperature of 25°C, the reaction time of 1,1-DNE was 0.8 μ sec at 90 kbar, whereas the reaction time of 1,1,1-FDNE was greater than 4 μ sec (failed to detonate) at 97 kbar (see Figure 6). In both these comparisons, namely, 1,1-DNP versus 2,2-DNP, and 1,1-DNE versus 1,1,1-FDNE, the compound with no α -hydrogen was less reactive than the compound that had a hydrogen atom α to the dinitro group.

Finally, the results for methyl nitrite and 1,1-DNP show that increasing the preshock temperature reduces the shock pressure required for a given reaction time (see Figures 7 and 8). This is in line with previous observations⁵ and is attributed to an increase in shock temperature as the preshock temperature is increased.

C. Detonation Failure

One of the unexplained features of detonation failure is a model that will satisfactorily explain the features of dark waves. In the hope of understanding the subject, we have begun to make dark wave experiments on dinitroalkanes. In some previous work with difluoroaminoalkanes⁷, we recorded imprints of failure waves on a brass cone (see Figures 9 and 10) using 1,2-bis(difluoroamino)-2-methylpropane (IBA). In massive lead confinement, IBA had a failure diameter of 9.5 mm. In the same lead

^{*}1,1-DNE is balanced to CO, H₂O, and N₂, whereas 1,1-DNP is fuel-rich. Thus the amount of heat released per cc of 1,1-DNE will be greater than that for 1,1-DNP.



TA 8525 56

FIGURE 4 SMOOTH-SHOCK REACTION TIME MEASUREMENTS FOR 1,1-DNE AND 1,1-DNP AT A PRESOCK TEMPERATURE OF 25°C

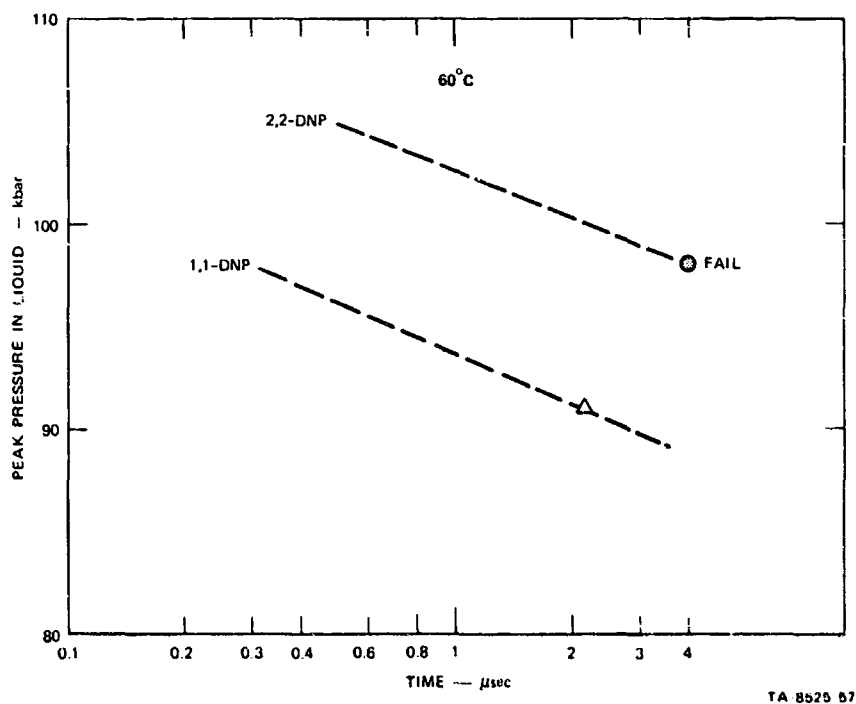
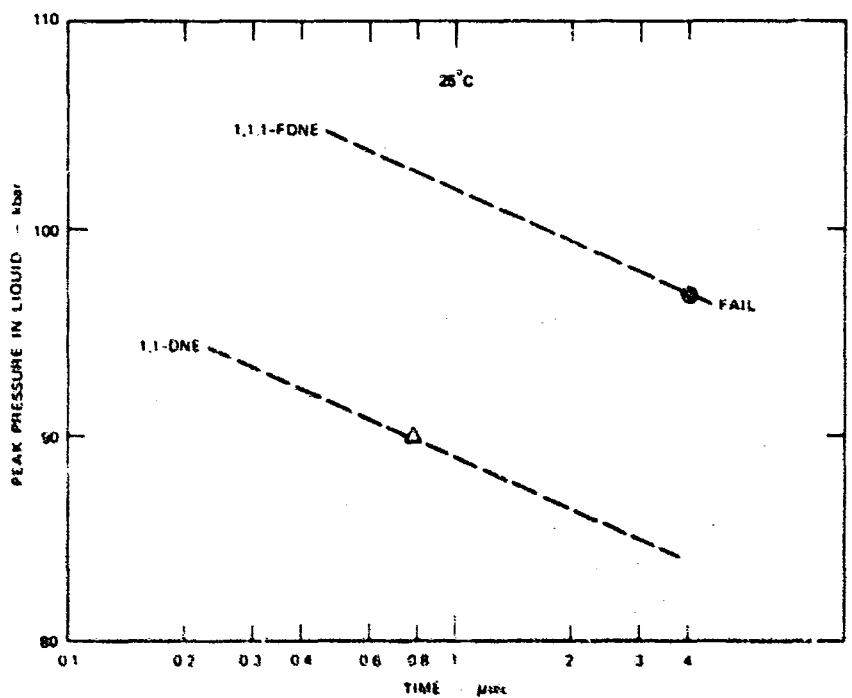


FIGURE 5 SMOOTH-SHOCK REACTION TIME MEASUREMENTS FOR 1,1-DNP AND 2,2-DNP AT A PRESOCK TEMPERATURE OF 60°C



1A 8526 68

FIGURE 6 SMOOTH-SHOCK REACTION TIME MEASUREMENTS FOR 1,1-DNE AND 1,1,1-FDNE AT A PRESOCK TEMPERATURE OF 25°C

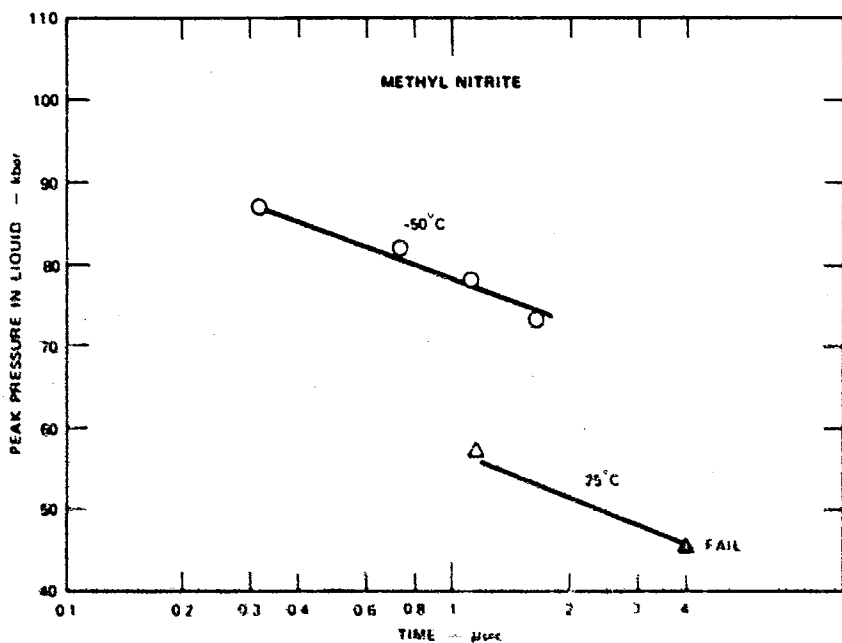
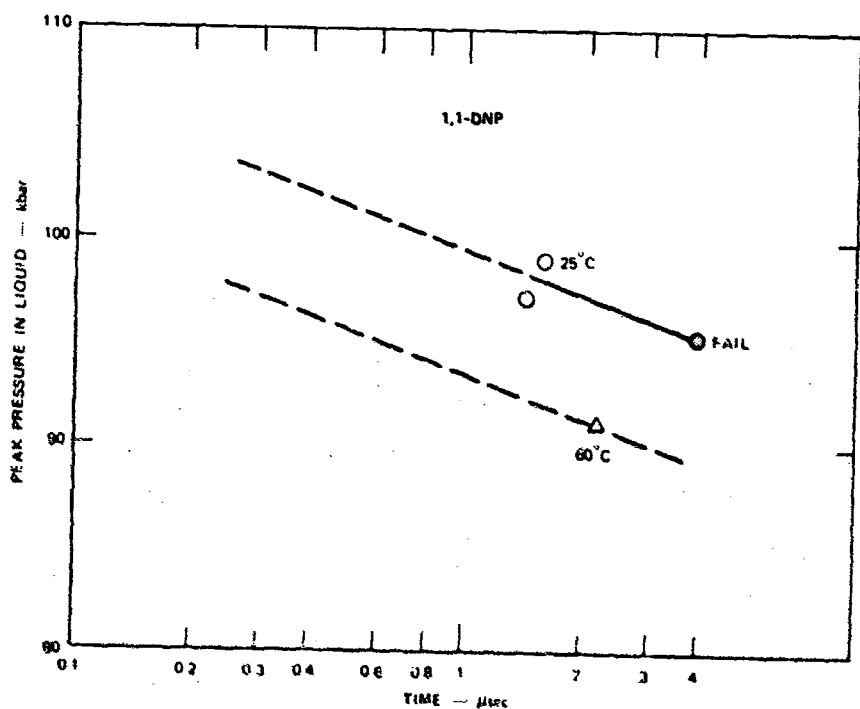
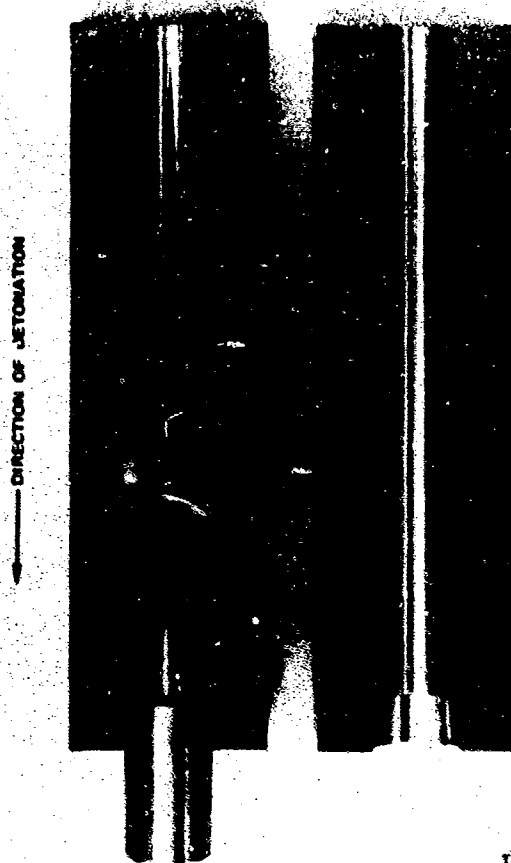


FIGURE 7 EFFECT OF PRESOCK TEMPERATURE ON SMOOTH-SHOCK REACTION TIME MEASUREMENTS FOR METHYL NITRITE



TA 6925 55

FIGURE 8 EFFECT OF PRESOCK TEMPERATURE OF SMOOTH-SHOCK REACTION TIME MEASUREMENTS FOR 1,1-DNP



TA-8828-22

FIGURE 9 BRASS CONE AND CYLINDER BEFORE FIRING. One-half actual size.



FIGURE 10 FAILURE WAVES EMBOSSED ON BRASS CONE BY DETONATION IN IBA.
The cone is rotated slightly in successive pictures.

Reproduced from
best available copy.

block apparatus the dinitroalkane with the closest failure diameter was 1,1-DNP (11 mm). We therefore chose 1,1-DNP for the brass cone experiments. The resulting imprints using 1,1-DNP are shown in Figure 11 and 12. The gross features for 1,1-DNP are similar to those observed for IBA, as might be expected because the gross physical properties of 1,1-DNP and IBA are similar, but a detailed explanation of the fine structure is still unavailable.

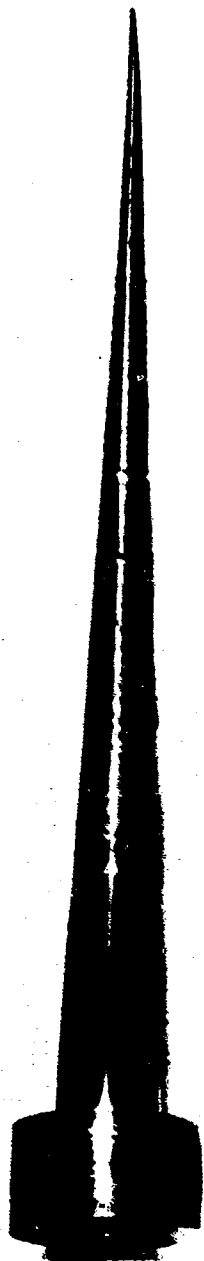
D. "Universal" Hugoniot for Liquids (with M. Cowperthwaite and R. W. Woolfolk)

In the 1970 Final Report,⁸ we discussed a "universal" Hugoniot for liquids that had the form

$$U_s/c_0 = 1.37 - 0.37 \exp[-u_p/c_0] + 1.62 u_p/c_0 \quad (1)$$

where U_s is the shock velocity, u_p is the particle velocity, c_0 is the sonic velocity, and u_j is a constant. In Figure 13 the experimental data are shown along with three curves that correspond to $u_j = \infty$, 5, and 1. The value of $u_j = \infty$ was used in shock temperature calculations because (1) it simplified the calculations, (2) we found that the values of shock temperature were not very sensitive to the value of u_j , and (3) the exact value of u_j was not known. However, u_j can not be infinite because in the limit, at $u_p = 0$, $U_s = c_0$. By observation of Figure 13, it appears that the value of u_j should be ≤ 5 . We have used two approaches to obtain a value for u_j . The first is based on thermodynamic relations of the Hugoniot and the isentrope, and the second is the direct experimental determination of the form of the Hugoniot in the region of 0 to 10 kbar.

— DIRECTION OF DETONATION



— DIRECTION OF DETONATION



TA-8525-68

FIGURE 11 FAILURE WAVES EMBOSSED ON TWO SIDES OF BRASS CONE AFTER DETONATION OF 1,1-DINITROPROPANE

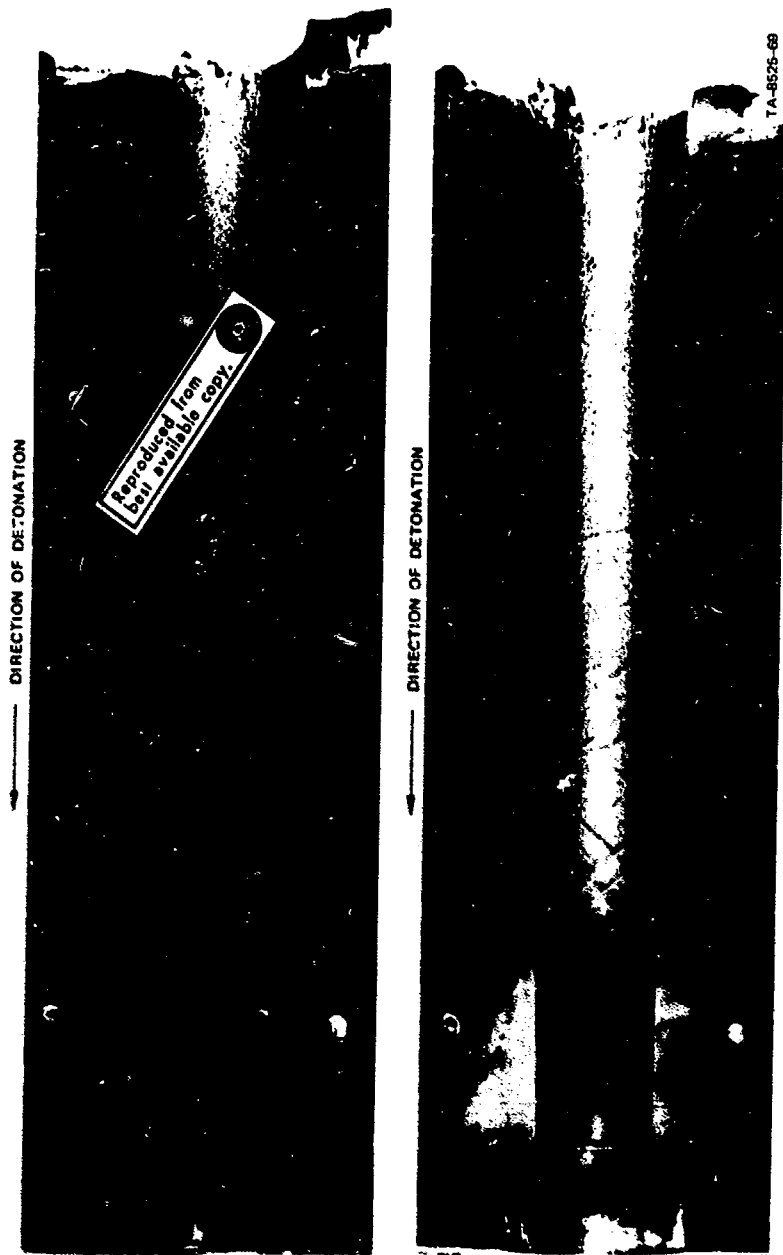


FIGURE 12 FAILURE WAVES EMBOSSED ON TWO HALVES OF BRASS CYLINDER AFTER DETONATION OF 1,1-DINITROPROPANE

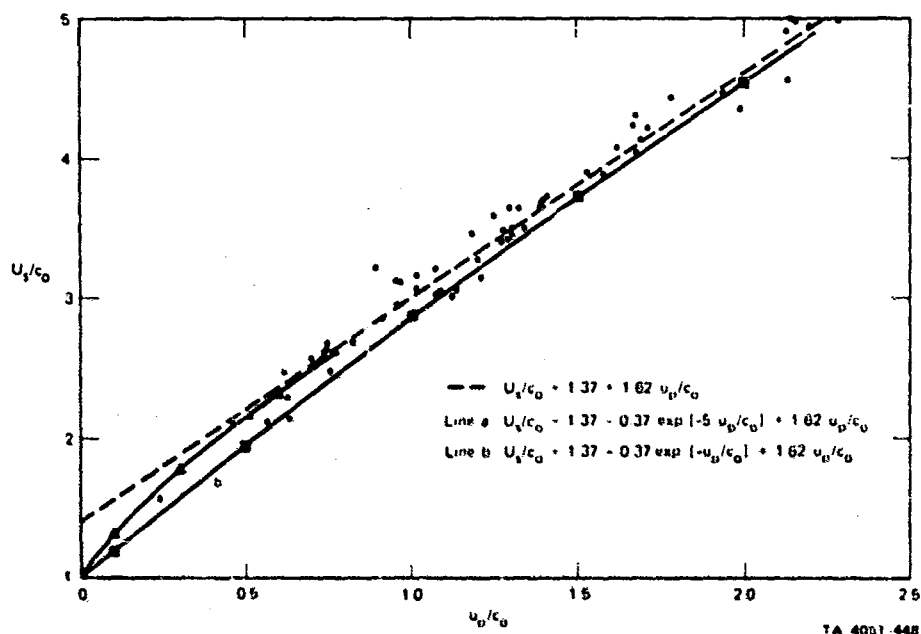


FIGURE 13 NORMALIZED U_i-u_D PLOT

The thermodynamic approach is as follows. Transposing c_o in equation (1) and differentiating U_s with respect to u_p ,

$$\frac{dU_s}{du_p} = 0.37 u_3 \exp[-u_3 u_p / c_o] + 1.62 \quad (2)$$

when $u_p \rightarrow 0$,

$$\frac{dU_s}{du_{p_o}} \rightarrow 0.37 u_3 + 1.62 \quad (3)$$

that is,

$$u_3 = \left(\frac{dU_s}{du_{p_o}} - 1.62 \right) / 0.37 \quad (4)$$

The problem is then to find dU_s/du_{p_o} . At $p = 0$ it can be shown from thermodynamics that

$$\left(\frac{dU_s}{du_p} \right) = \frac{v_o^{-1}}{4c_o^2} \left(\frac{\lambda^2 p}{\lambda v^2} \right)_s \quad (5)$$

Now

$$\left(\frac{\lambda p}{\lambda v} \right)_s = - \frac{c^2}{v^2} \quad (6)$$

And differentiating with respect to v ,

$$\left(\frac{\lambda^2 p}{\lambda v^2} \right)_s = \frac{2c}{v^2} \left[\frac{c}{v} - \left(\frac{\lambda c}{\lambda v} \right)_s \right] \quad (7)$$

Further,

$$\left(\frac{\partial c}{\partial v}\right)_s = \left(\frac{\partial c}{\partial v}\right)_p + \left(\frac{\partial c}{\partial p}\right)_v \left(\frac{\partial p}{\partial v}\right)_s \quad (8)$$

$$= \left(\frac{\partial c}{\partial v}\right)_p \left[1 + \left(\frac{\partial v}{\partial c}\right)_p \left(\frac{\partial c}{\partial p}\right)_v \left(\frac{\partial p}{\partial v}\right)_s \right] \quad (9)$$

$$= \left(\frac{\partial c}{\partial v}\right)_p \left[1 - \left(\frac{\partial v}{\partial p}\right)_c \left(\frac{\partial p}{\partial v}\right)_s \right] \quad (10)$$

$$= \left(\frac{\partial c}{\partial v}\right)_p \left[1 + \frac{c^2}{v^2} \left(\frac{\partial v}{\partial p}\right)_c \right] \quad (11)$$

If $(\partial c/\partial v)_p$ and $(\partial v/\partial p)_c$ were known at $p = 0$, substitution into equations (11), (7), (5), and (4) would yield a value for u_3 . We have used data from echo-sounding tables for pure water,⁹ together with p - v - T data,¹⁰ to construct a graph of the variation of sound speed with specific volume at pressures of 1, 50, 100, and 150 bar (see Figure 14). At $p = 1$ bar, $T = 25^\circ\text{C}$, $c = 1493$ m/sec, from the graph, $\left(\frac{\partial c}{\partial v}\right)_{p=1} = \left(\frac{\Delta c}{\Delta v}\right)_{p=1} = 1.027 \times 10^6 \text{ g/}(\text{sec cm}^2)$. Similarly, from the graph, at constant $c = 1493$ m/sec, the following values of p and v were read off:

p (bar)	v (cc/g)	Δv (cc/g)
1	1.00295	0.00325
50	0.99970	0.00290
100	0.99680	0.00275
150	0.99405	

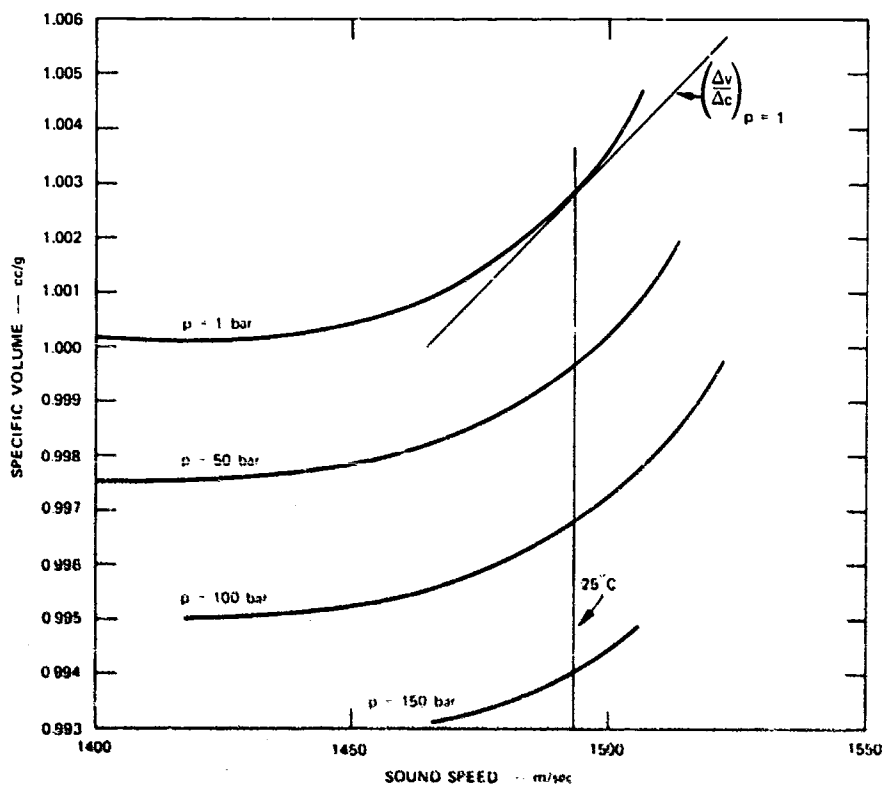


FIGURE 14 SOUND SPEED IN PURE WATER AS A FUNCTION OF SPECIFIC VOLUME AT PRESSURES OF 1, 50, 100, AND 150 bar

Extrapolating to $p = 1$, we obtain

$$\left(\frac{\partial v}{\partial p}\right)_c = \left(\frac{\Delta v}{\Delta p}\right)_c = -7 \times 10^{-11} \text{ cm}^5/(\text{dyne g})$$

Substitution of $c = 1.493 \times 10^5 \text{ cm/sec}$, $v = 1.00295 \text{ cm}^3/\text{g}$, $(\partial v/\partial p)_c = -7 \times 10^{-11} \text{ cm}^5/(\text{dyne g})$ and $(\partial c/\partial v)_p = 1.027 \times 10^6 \text{ g}/(\text{sec cm}^2)$ into equation (11) gives $(\partial c/\partial v)_s = 5.66 \times 10^5 \text{ g}/(\text{sec cm}^2)$. Substitution into equation (7) gives $(\partial^2 p/\partial v^2)_s = 2.12 \times 10^{11} \text{ sec}^2/(\text{g}^3 \text{ cm}^{-7})$; substitution into equation (5) gives $(dU_s/du_p) = 2.40$. Finally, substitution into equation (4) gives $u_3 = 2.1$.

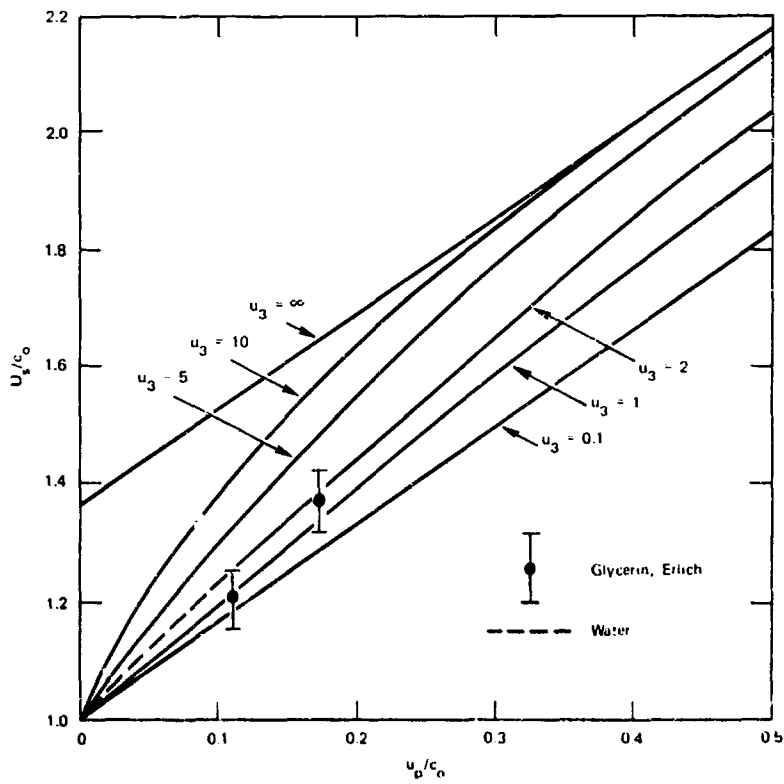
The region of Figure 13 close to the origin has been replotted as Figure 15, using equation (1) and values of $u_3 = \infty, 10, 5, 2, 1$, and 0.1 . Also plotted in Figure 15 are two experimental Hugoniot points for glycerine, obtained by Dr. D. Erlich of SRI. Until further data are available, we conclude that a value of $u_3 = 2$ is consistent with results of the calculations on water and with the experimental data on glycerin. In other words, equation (1) becomes:

$$U_g/c_o = 1.37 - 0.37 \exp[-2u_p/c_o] + 1.62 u_p/c_o \quad (12)$$

E. Publications

The following papers resulting from this work have been accepted for publication or presentation:

1. "Heat Capacities of Some Dinitroalkanes," W. E. Robbins and R. Shaw, J. Chem. Thermodynamics.
2. "Thermal Decomposition of Nitromethane and Some Dinitroalkanes at Static High Pressure of 1 to 50 kbar," E. L. Lee, H. D. Stromberg, P. S. DeCarli, D. S. Ross, and R. Shaw, Western States Section of the Combustion Institute Spring Meeting, Seattle, 24 to 25 April 1972.



TA 8525-60

FIGURE 15 CALCULATED NORMALIZED U_1-u_D PILOTS FOR VALUES OF $u_3 = 0.1, 1, 2, 5, 10$, AND ∞ , AND SHOWING ERLICH'S EXPERIMENTAL GLYCERIN DATA

F. Future Work

During the next few weeks we plan to extend the shock initiation and static high-pressure experiments on the dinitroalkanes with emphasis on the β -hydrogen effect. During the summer we plan to devote more attention to the problems of dark waves and Dremen's failure diameter theory.

G. Acknowledgments

G. S. Cartwright was the site leader on the shock initiation experiments. The pressure reaction cell for the methyl nitrite shot was made by J. H. Hannigan with help from J. W. Van Gastel. I am indebted to S. J. Jacobs of Naval Ordnance Laboratory and to C. L. Mader and J. N. Zinn of Los Alamos Scientific Laboratories for many helpful discussions. We thank David F. Barnes of the U.S. Geological Survey for providing echo-sounding data, and David C. Erlich for permission to quote his unpublished results on glycerin.

III LOW-VELOCITY DETONATION

(R. W. Woolfolk)

A. Introduction

This part of the Sensitivity Fundamentals program deals with the occurrence of low-velocity detonation (LVD) in model dinitroalkanes that are related to useful high energy plasticizers. In particular, we are studying the relationship between chemical structure and LVD sensitivity. Our recent efforts have concentrated on those chemical and physical properties that influence the LVD gap sensitivity of materials, especially the thermodynamic and kinetic properties.

LVD is defined as a reaction wave propagating at a velocity supersonic with respect to the unreacted liquid but slower than a conventional high-velocity detonation (HVD). We believe that the LVD wave is propagating in a cavitated fluid and that the production of this cavitation is an important process in the initiation and propagation of LVD. Compared with HVD, the LVD process is a far more complex phenomenon, which indicates why a quantitative model for LVD has yet to be suggested.

In our studies of LVD we have used model compounds and are currently working on the dinitroalkanes. The LVD behavior of the dinitropropanes and the dinitroethanes are in marked contrast to their low-pressure reaction rates. The propanes, 1,1-DNP and 2,2-DNP, cannot be initiated to LVD in our tests, but 1,1-DNE can. Since we have shown¹¹ in our low-pressure experiments that these dinitroalkanes have substantially the same rate parameters for decomposition, the explanation for their diverse LVD behavior must lie elsewhere.

Because of the need to produce cavitation ahead of the reaction zone, the energy requirement in LVD propagation may be greater than that required for a conventional detonation. Therefore, we have been examining the

energy release expected from an LVD reaction and comparing this energy with LVD behavior to determine if there is a minimum energy required for the propagation of LVD. To estimate the available energy, we have been using TIGER, a computer code designed for thermodynamic and hydrodynamic calculations at high pressures. We have also begun work on pressure-time relations in LVD.

B. TIGER Calculations

The TIGER program calculates not only the amounts of all important equilibrium products at a desired temperature and pressure but also selects which of the possible products are present at equilibrium providing the product is listed in the program library. Thus, CF_4 is not an important equilibrium product from IBA under any conditions used in the calculation (Figure 17).

The TIGER studies have been extended to include the difluoramino alkanes previously studied and 1,1,1-fluorodinitropropane (FDNP). We wanted to compare the energy release for all these materials and to study how the product distribution changed with pressure and temperature. We estimated that the LVD reaction would take place in the 10 to 20 kbar region and in the temperature range 1000 to 3000°K (more likely in the range 1000 to 2000°K). Figures 16 through 20 show the equilibrium product distribution as calculated by TIGER for 1,2-DP, IBA, 1,1-DNE, 1,1-DNP, and 1,1,1-FDNP. These results are all at 20 kbar. For comparison Figure 21 and 22 show the corresponding distribution at 10 kbar for IBA and 1,1-DNE. A comparison of the figures for 1,1-DNE and IBA shows that the effects of pressure are very slight. In the difluoramino case, temperature also has little effect on the product distribution. For 1,1-DNE and, in fact, for all dinitroalkanes thus far studied, the variation of products with temperature is much greater than with pressure in the ranges of interest.

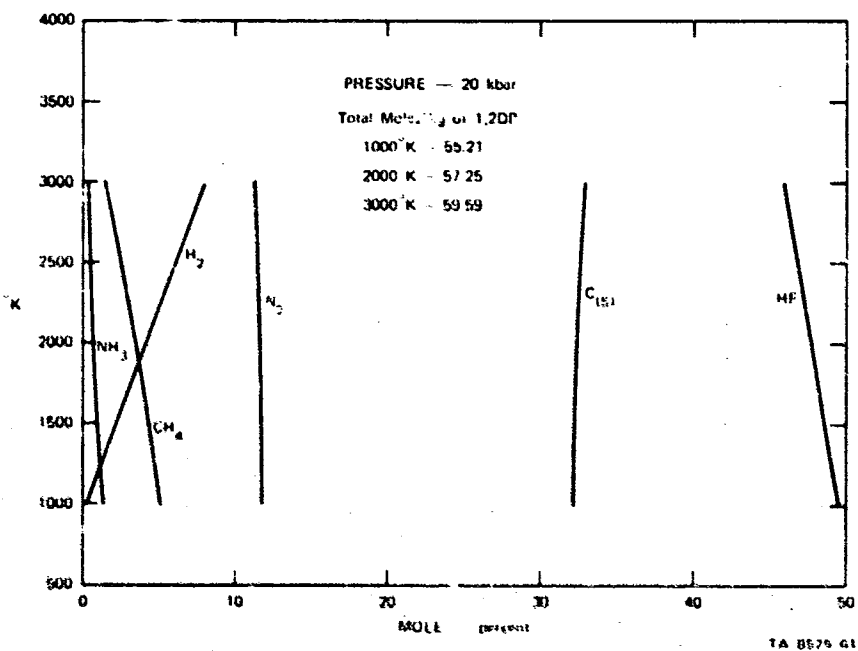


FIGURE 16 MOLE PERCENT AS A FUNCTION OF TEMPERATURE FOR 1.2 DP (Tiger)

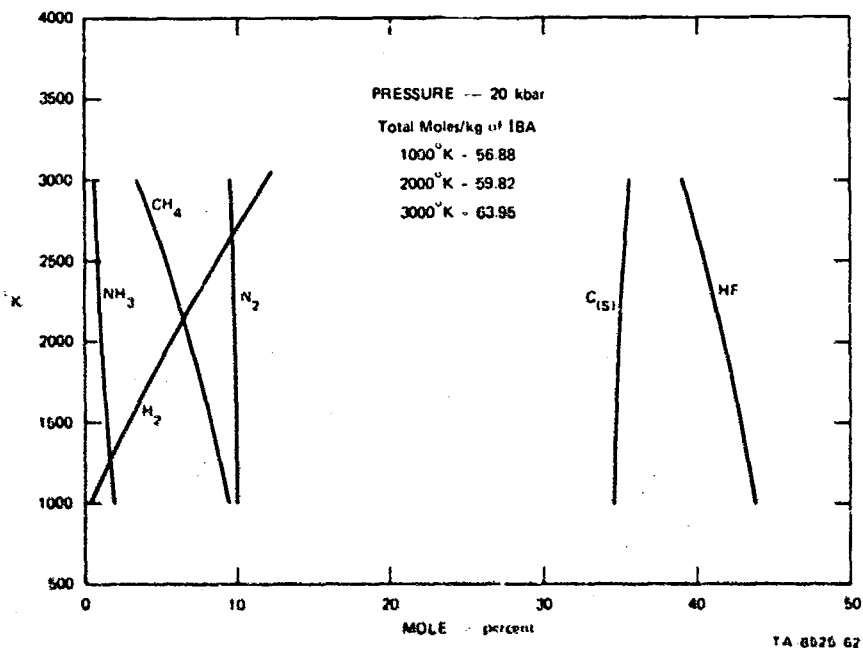


FIGURE 17 MOLE PERCENT AS A FUNCTION OF TEMPERATURE FOR IBA (Tiger)

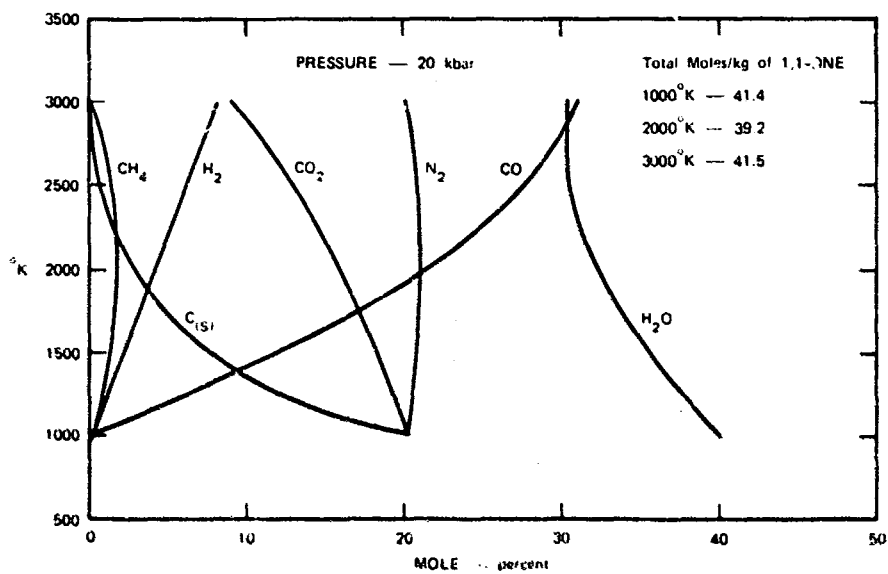


FIGURE 18 MOLE PERCENT AS A FUNCTION OF TEMPERATURE FOR 1,1-DNE (Tiger)

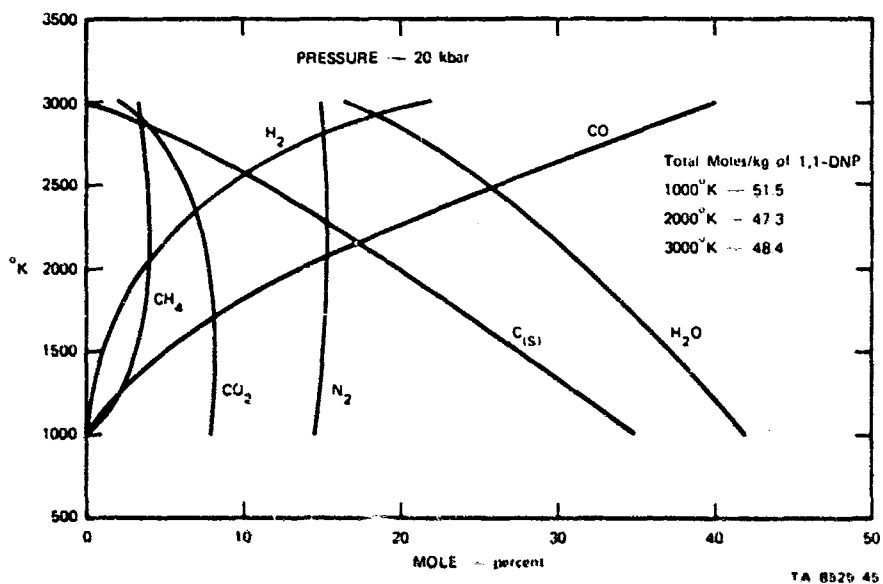


FIGURE 19 MOLE PERCENT AS A FUNCTION OF TEMPERATURE FOR 1,1-DNP (Tiger)

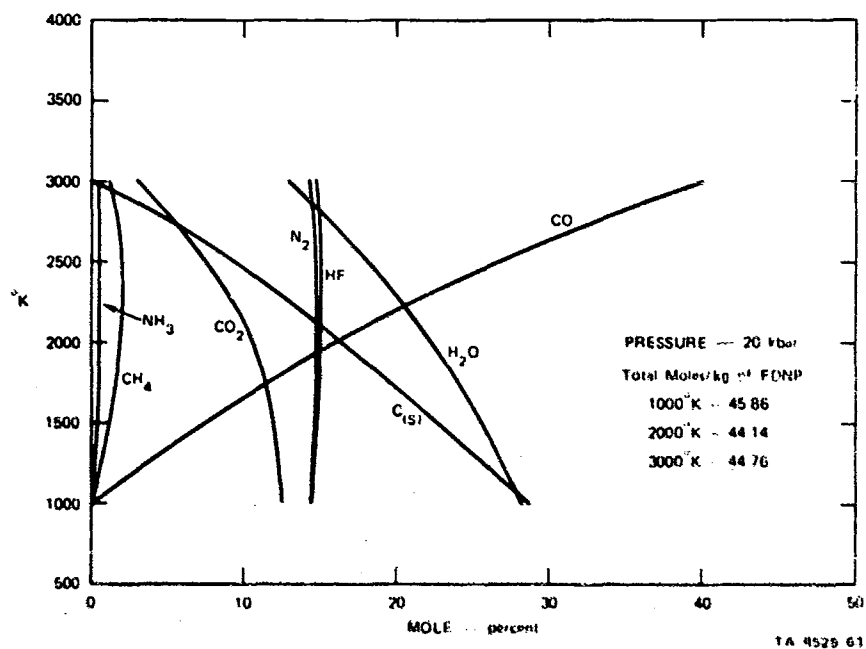


FIGURE 20 MOLE PERCENT AS A FUNCTION OF TEMPERATURE FOR 1,1,1-FDNP (TIGER)

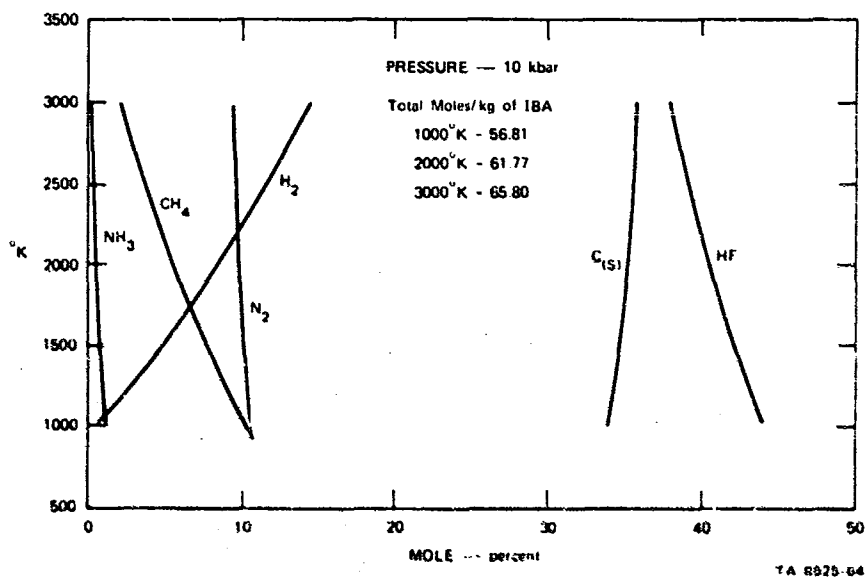


FIGURE 21 MOLE PERCENT AS A FUNCTION OF TEMPERATURE FOR IBA AT 10 kbar (Tiger)

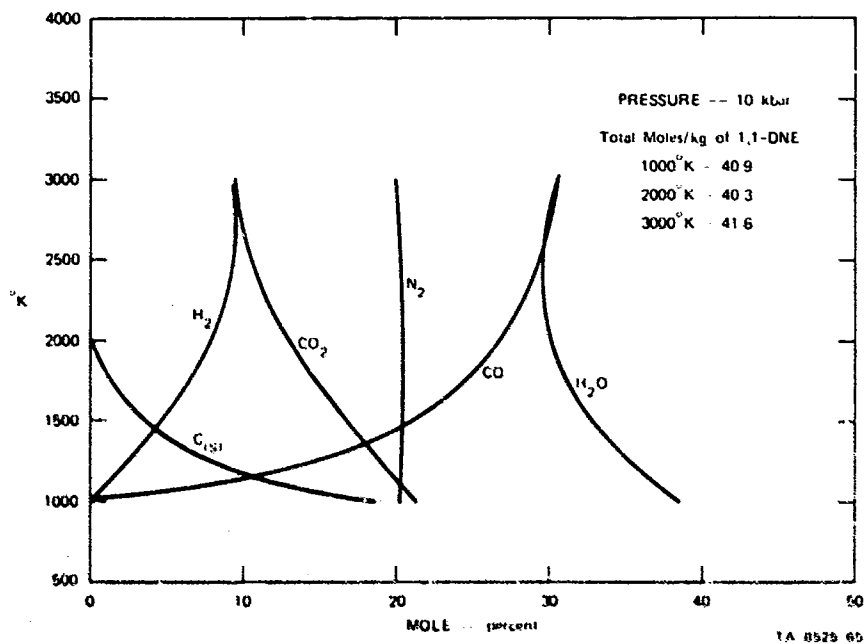


FIGURE 22 MOLE PERCENT AS A FUNCTION OF TEMPERATURE FOR 1,1-DNE AT 10 kbar (Tiger)

An examination of the results of the TIGER calculation shows that the presence of fluorine in the material has a strong effect on the change of energy release with temperature. Because HF is so stable compared with other fluorine-containing products, changing the temperature does not shift its equilibrium concentration as it does for H-C-O systems. Table III lists many of the compounds for which we have estimated the heat of reaction using TIGER. We have also tested most of these materials for LVD. In Table III we have calculated the ratio of the heat of reaction, ΔH_r , to the heat of vaporization, ΔH_v . We have felt for some time that because cavitation plays an important role in LVD, ΔH_v should also be an important parameter. In the past we have tried to correlate on a quantitative basis the LVD gap sensitivity with the ratio $\Delta H_r/\Delta H_v$, and as we pointed out in the last report,⁶ the correlation was not able to differentiate between 1,1-DNP and 1,1-DNE, whose LVD behavior is very different. However, when we compare the ratios as shown in Table III with the LVD sensitivities a pattern does emerge. Table IV lists the LVD gap sensitivities of these materials and their values of $\Delta H_r/\Delta H_v$ as estimated by TIGER.

At 20 kbar and 2000°K, the ratio $\Delta H_r/\Delta H_v$ shows the following order as seen in Tables III and IV: NM < 1,1-DNP < 1,1-DNE < EN < IBA < 1,2-DP < 2,2-DP. With the exception of EN, which is less sensitive than 1,1-DNE, this is the same order as the LVD gap sensitivity. The small difference in $\Delta H_r/\Delta H_v$ for 1,1-DNP and 1,1-DNE means that other factors must determine LVD gap sensitivity in these materials. We know from our low-pressure gas-phase kinetic studies that these two materials react at the same rate.⁷ Therefore, the explanation cannot lie with low-pressure initiation kinetics. The static high-pressure studies have not yet been completed on 1,1-DNE, so we do not know if it will react faster than 1,1-DNP at high pressure.

Because this boundary between no LVD and LVD for 1,1-DNP and 1,1-DNE exists, we should be able to find a mixture of these compounds for which LVD will occur and by using TIGER, estimate the energy of that mixture.

Table III

CALCULATED ENERGY RELEASE FOR SELECTED COMPOUNDS AT 20 kbar

Compound	Density (25°) (g/cc)	ΔH_v (25°) ^a (kcal/mole)	Temp (°K)	ΔH_r	$ \Delta H_r / \Delta H_v $	
				(kcal/mole)		
NM	1.13	9.09	1000	-88	9.7	
NM			2000	-74	8.05	
1,1-DNF	1.254	14.9	1000	-182	12.2	
1,1-DNP			2000	-162	10.9	
1,1-DNE	1.355	13.9 ^b	1000	-175	12.1	
1,1-DNE			2000	-155	11.1	
EN ^c	1.10	8.7	1000	-121	13.8	
EN			2000	-111	12.8	
IBA	1.213	8.9	1000	-223	25.2	
IBA			2000	-225	25.0	
1,2-DP	1.265	7.9	1000	-225.5	28.3	
1,2-DP			2000	-225.5	28.3	
2,2-DP	1.254	7.0	1000	-225.5	32.2	
2,2-DP			2000	-225.5	32.2	
1,1,1-FDNP	1.328	15 est ^d	1000	-201.2	13.4	
			2000	-180.8	12.0	

a. Obtained from the vapor pressure curves.

b. Estimated from 1,1-DNP using group additivity.

c. EN = ethyl nitrate.

d. Estimated from 1,1-DNP.

Table IV
LVD GAP SENSITIVITIES AND $\Delta H_r/\Delta H_v$ AT 2000°K AND
20 kbar FOR SELECTED COMPOUNDS

Compound	$\Delta H_r/\Delta H_v$	LVD Gap Sensitivity (cm Plexiglas)
NM	8.05	No LVD
1,1-DNP	10.9	No LVD
1,1-DNE	11.1	6.4-8.3 ^a or b
EN	12.8	3.0-3.8 ^a or b
IBA	25.0	16-17 ^a or b
1,2-DP	28.3	30-40 ^a 91-127 ^b
2,2-DP	32.2	>180 ^b
1,1,1-FDNP	12.0 est.	Not yet tested

^a Without witness plate.

^b With witness plate.

This may give us an insight as to the validity of the hypothesis of a critical energy for LVD.

We have included the estimated value for 1,1,1-FDNP where an F atom has replaced an H atom. Because of the stability and energy content of HF, 1,1,1-FDNP gives a higher ΔH_r than 1,1-DNP. If our hypothesis about critical energy is valid, it means that 1,1,1-FDNP might exhibit LVD if other factors are equal. The HVD failure diameters of these two materials are very similar.⁷ We did not have enough 1,1,1-FDNP available to determine either its HVD reaction time or LVD sensitivity. Therefore, we could not compare these parameters as we did for the difluorominoalkanes. We do have, however, sufficient 1,1,1-FDNE, the ethane isomer, to make these tests for comparison. We will do this as well as run TIGER calculations on the 1,1,1-FDNE.

C. Experimental Work

Experimental work has been limited by the lack of explosives and the lack of a test site. Both these problems are now corrected. The tetryl explosive will be delivered in a few weeks, and the framing camera necessary for our LVD gap studies is now in working order at our new test site. All the materials have been prepared for testing. These include 1,1-DNE and 1,1,1-FDNE. Since 1-fluoro-1,1-dinitroethanol, a compound that we may want to test, can be obtained commercially, we will not have to prepare it. With all systems prepared, we will have a very full schedule this spring.

D. Pressure-Time Studies

We have recently begun studies of LVD initiation and propagation in which we monitor the pressure-time history of the liquid and container walls. This work is a continuation of studies that were conducted for AFOSR. In that program SRI developed a method for studying the pressure-time history in the liquid during LVD. We hope to use this method to study 1,1-DNE, EN, and other LVD materials. This should give us an estimate of the pressure in the liquid and also indicate how the energy is distributed between the walls and the liquid. Our initial studies in conjunction with the AFOSR were only a partial success as the material chosen did not undergo LVD because of excess solvent. This will be corrected on the next shot.

This technique uses a manganin gage whose resistance is a function of pressure. By monitoring this resistance during shock initiation, we can determine the pressure level in the liquid at all phases of the LVD reaction. By locating these gages at various points in the tube, we can ascertain how the pressure varies along the tube as well as the time history at any one point. Figure 23 depicts what a typical result might look like.

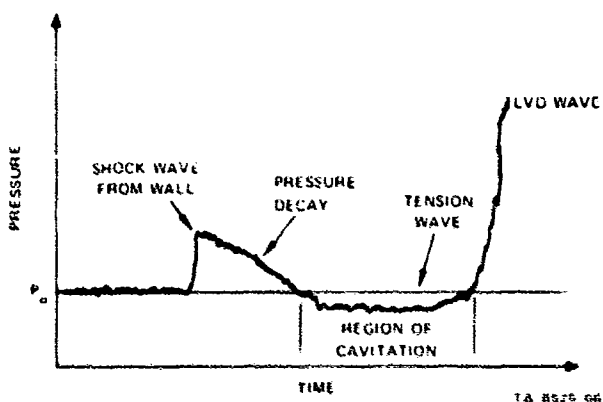


FIGURE 23 TYPICAL PRESSURE-TIME HISTORY FOR SHOCKED LVD LIQUID

E. Future Work

During the next period we will determine the LVD gap sensitivity of 1,1-DNE at various temperatures and the LVD gap sensitivity of 1,1,1-FDNE at ambient temperature. In addition, we are planning to use 1,1-DNE and a plasticizer in our study of the pressure history of LVD initiation and propagation. Part of these last studies will be completed in mid-April.

Mixtures of 1,1-DNP and 1,1-DNE will also be tested for LVD to determine the composition that exhibits LVD.

Other fluorodinitro compounds will be tested if the results from the 1,1,1-FDNE studies prove interesting. These may include 1-fluoro-1,1-dinitroethanol since we know from previous studies that fluorodinitroethyl formal (FEFO) is moderately sensitive to LVD. Since 1,1-DNE is fairly insensitive to LVD, this series should make an interesting comparison.

IV STATIC HIGH-PRESSURE AND KINETIC EFFECTS (R. Shaw, P. S. DeCarli, and D. S. Ross of SRI, and E. L. Lee and H. D. Stromberg of LLL)

A. Introduction

In our last report⁶ we described our static high-pressure (SHP) experimental technique and reported results for NM over a range of pressures from 1 to 50 kbar. In this range there was a decrease in the time to explosion with increasing pressure.

In this report we present data from SHP experiments done both at SRI and at LLL on four dinitropropanes--1,1-DNP, 1,1,1-FDNP, 2,2-DNP, and 1,2-DNP and discuss the problem of "high" Arrhenius parameters obtained in these experiments. Finally, we present the final results obtained in the very low-pressure pyrolysis (VLP) experiments done on the same four dinitropropanes.

B. Static High-Pressure Experiments

These experiments are at a very interesting stage, particularly when taken in conjunction with the shock initiation experiments (Section II). Since the last report we have completed experiments at SRI on 1,1-DNP at 1 and 10 kbar, and on 1,1,1-FDNP at 10 kbar. At LLL, experiments have been made on 1,2-DNP and 2,2-DNP¹² at 10 and 50 kbar. The results are given in Table V. Thermal explosion times as a function of temperature for several dinitroalkanes at 10 kbar are shown in Figure 24.

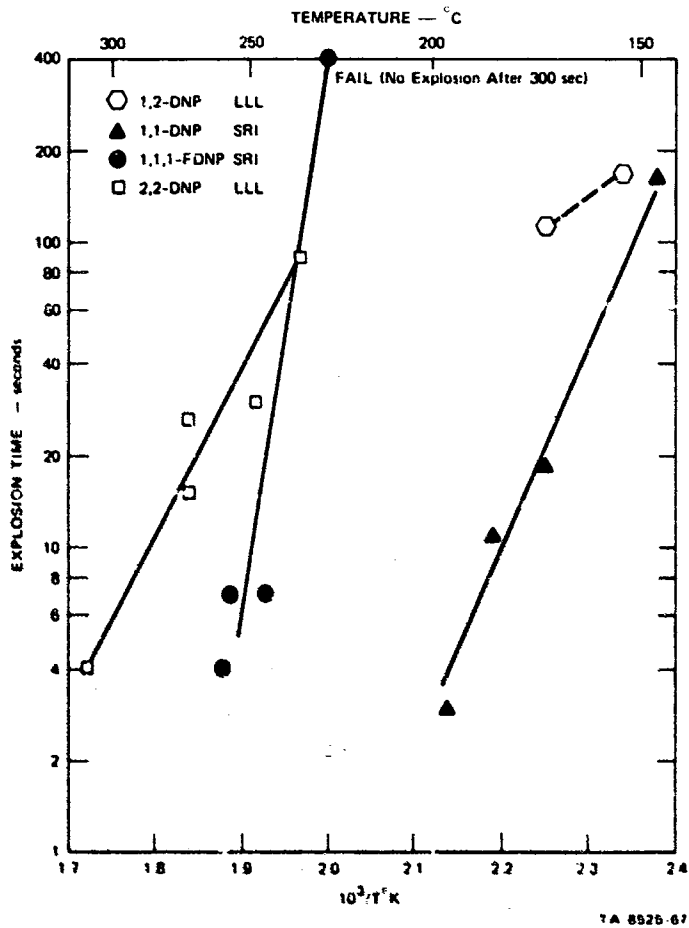


Table V

THERMAL EXPLOSION TIMES
OF DINITROALKANES AT STATIC HIGH PRESSURES

Compound	Lab	1 kbar		10 kbar		50 kbar	
		Temp. (°C)	Explosion Time (sec)	Temp. (°C)	Explosion Time (sec)	Temp. (°C)	Explosion Time (sec)
1,2-DNP	LLL			173	112	173	1
				154	170	154	20
						135	82
1,1-DNP	SRI	184	>200	195±5	3		
		204	10	184±2	11		
		209	1	173±2	18.5		
				147±2	165		
1,1,1-FDNP	SRI			260	4		
				256	7		
				246	7		
				228	>300		
2,2-DNP ^a	LLL			309	4	345	11
				270	15	316	18
				270	26	316	22
				248	30	302	20
				235	90	283	50
						259	100
						259	120

^a Reference 12.

The α -hydrogen effect found in measurements of smooth-shock reaction times is again apparent. In Figure 24, the compounds clearly fall into two sensitivity classes: 2,2-DNP and 1,1,1-FDNP, with no α -hydrogens, are significantly less sensitive than 1,2- and 1,1-DNP, which have α -hydrogens. Moreover, within the latter pair, although the data are a bit sparse, it would appear that 1,1-DNP is more sensitive than 1,2-DNP.

The effect of pressure changes on the reaction times is apparent from Table V, and displays another aspect of the α -hydrogen effect. Thus for 2,2-DNP an increase in the pressure increases the time to explosion, while for 1,2-DNP and 1,1-DNP a pressure increase decreases the time to explosion.

A puzzling feature of the results at 10 kbar with 1,1,1-FDNP is the very sharp increase in explosion time (from 7 sec to >300 sec) for a small decrease in temperature (Figure 24). This result is very similar to the behavior of nitromethane at 1 kbar discussed in the last report.⁶ During the current period we have given considerable thought to this problem.

There is the question of how to derive Arrhenius parameters for the global heat-releasing chemical reactions from the observed data--thermal explosion times as a function of temperature. Following Zinn and Mader's treatment,¹³ it is clear that one can not simply use the slope of the (explosion-time/reciprocal-temperature) plot to obtain the activation energy. The method of deriving Arrhenius parameters is more complex than that, although there is a rough correlation in that the steeper the explosion-time/reciprocal-temperature graph, the higher the apparent activation energy. The details of the calculations are given in a paper accepted for presentation at the Western States Spring Meeting of the Combustion Institute to be held in Seattle, 24-25 April 1972.

The results of such a computation for nitromethane yield an activation energy of 127 kcal/mole and the Arrhenius A-factor of 10^{40} sec^{-1} .

The problem then is with the "high" Arrhenius parameters. The term "high" is used because the activation energy of 127 kcal/mole is so much greater than the strength of the weakest bond, $D(\text{CH}_3\text{-NO}_2) = 60 \text{ kcal/mole}$. Usually activation energies are equal to, or less than, the strength of the weakest bond. A chain mechanism or catalyzed decomposition will tend to reduce an activation energy below the bond strength. Similarly, the A-factor is over twenty orders of magnitude higher than for a simple unimolecular or chain reaction.

"High" activation energies have been observed before. Maksimov¹⁴ and Rogers¹⁵ attributed "high" activation energies for decomposition of explosives to melting. The theory is that organic solids decompose faster in a molten state than as solids. So just below the melting point, the explosive is solid and stable. The temperature is raised a few degrees to the melting point, the explosive melts, and begins to decompose rapidly. This big difference in rate over a few degrees corresponds to a high activation energy. Unfortunately, the "high" activation energy for nitromethane is obtained at 1 kbar where the range is 340 to 380°C, and not at 10 kbar where the temperature is lower, namely, 227 to 310°C. This is, the nitromethane is much more likely to be solid at 10 kbar than 1 kbar, since Rabinovitch and Gorbushenkov¹⁶ have shown that the critical temperature of nitromethane is 315°C.

C. VLPP of Nitroalkanes (with Leonard Piszkwicz)

We previously reported the kinetic parameters for VLPP of several dinitroalkanes.⁴ We have now completed a study of the products of decomposition in VLPP for these same compounds. Together, these data serve as a point of reference for future considerations of mechanisms

Table VI

VLPP PRODUCTS FROM DINITROPROPANES^a

Compound	Products ^b	Relative Yield (%) ^c (±5%)
2,2-DNP	Acetone	55
	2-Nitropropene	45
1,1-DNP	Propionaldehyde	20
	trans-1-Nitropropene	5
	Unknown ^d	50
	Other minor products	5
1,1,1-FDNP	Propionyl fluoride	sole product ^e
1,2-DNP	trans-1-Nitropropene	75
	2-Nitropropene	25

^a Flow through reactor 10^{13} - 10^{16} molecules/sec.

^b The product distributions were reasonably constant over the range of decomposition studied.

^c The mass balances for 1,1-DNP, 2,2-DNP, and 1,2-DNP were estimated to be 90%. (see note e.)

^d The unknown was unstable; its behavior and vpc retention time suggest it to be nitroethylene.

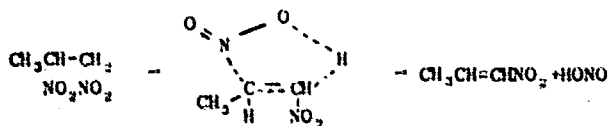
^e The mass balance in this case was about 10%. The poor result is due to the high volatility of propionyl fluoride, which results in a low trapping efficiency in these experiments.

of decomposition in the SHP region and complete our VLPP study of nitroalkanes. Results will be submitted for publication in the Journal of the American Chemical Society.

The kinetic parameters for unimolecular decomposition of the four dinitroalkanes examined in our earlier work⁶ are consistent with two kinds of mechanisms: a cyclic 5-center elimination of HONO from 1,2-DNP and C-N scission in the case of 1,1-DNP, 2,2-DNP, and 1,1,1-FDNP where geminate substitution weakens the C-N bond.

Products from VLPP, shown in Table VI, support these conclusions.

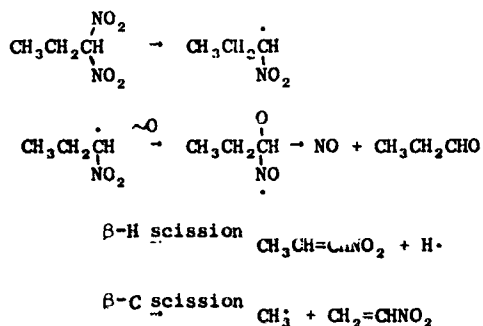
Two processes are significant. First, for 1,2-DNP, the isolation of the two nitroolefins indicates that, in agreement with the kinetic results, the compounds behaves like a simple mononitroalkane and eliminates HONO in a cyclic process.



The gem-dinitrocompounds, on the other hand, yield, in addition to olefins, carbonyl compounds. This result suggests that C-N scission is the dominant mode of decomposition for these compounds in accord with the results by Nazin et al.¹⁷

The carbonyl products can be explained by a mechanism including initial C-N scission followed by intramolecular migration of oxygen from N to C. In the case of 1,1,1-FDNP, this route apparently is the only one followed. For 2,2- and 1,1-DNP, however, the formation of

nitroolefin indicates that β -scission is occurring. For 1,1-DNP



The migration of O is reminiscent of F migration in the case of the difluoroaminoalkane 2,2-DP.⁸ However, while the rearrangement is about 40 kcal/mole exothermic in the fluorine case, it is roughly thermo-neutral in the oxygen case.

For 1,1-DNP it was shown that the product distribution was essentially unchanged for the three reactor exit apertures, or a change in wall collisions by a factor of over 100. Thus the reactions we are seeing are very likely true unimolecular reactions in the gas phase.

D. Future Work

Despite the unusually high kinetic parameters, the results of the SHP experiments are interesting in terms of the chemistry they suggest must be proceeding. The clear demonstration of an α -hydrogen effect is in accord with an initiation model in which either the aci-forms of the compounds are important to the detonation process, or, at the very least, the transfer of the α -hydrogen is a significant step.

A knowledge of the products formed in the initiation period is important as it would provide some insight into the critical molecular processes during this period. Although the present experimental set-up

is ideal for reaction time studies, attempts at product isolation have been unsuccessful for a number of reasons, not the least of which is the small sample volume of about 10 μ l. We plan to extend the current SHP work by carrying out thermal experiments at pressures in the 1-10 kbar range, on samples on the order of 100 to 500 μ l. The runs will be made at generally lower temperatures than those used in the current work, so that detonation will not occur and so that the intermediate products formed during this initiation period can be isolated and identified.

The planned work will use a new high pressure apparatus currently being assembled, and the details of the operation will be presented in the next report. Briefly, however, samples of the nitro compounds will be put into polyethylene or FEP "spaghetti" tubing and the ends heat sealed. The pressure chamber, filled with hydraulic fluid, will be large enough to accommodate one or more sample tubes. The sealed assembly will be pressurized and then heated externally for some suitable period. Then the sample tubes will be withdrawn and opened in a vacuum system suitably coupled to a gas chromatograph. In this way all the products, including any gases, will be isolated and identified.

REFERENCES

1. S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas-Phase Unimolecular Reactions," NSRDS-NBS 21, U.S. Government Printing Office, Washington, D. C., 1970.
2. S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, Chem. Rev. 69, 279 (1969).
3. D. R. Stull, E. F. Westrum, and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds (John Wiley and Sons, Inc., New York, 1959).
4. Handbook of Chemistry and Physics, 51st ed. Chemical Rubber Company, Cleveland, Ohio, (1970-71).
5. J. G. Berke, R. Shaw, D. Tegg, and L. B. Seely, Fifth Symposium on Detonation, Pasadena, California, 1970, p. 168.
6. P. S. DeCarli, D. S. Ross, R. Shaw, and R. W. Woolfolk, "Sensitivity Fundamentals," SRI Project 8525, Technical Progress Report 71-2 (Semiannual), September 1971.
7. D. S. Ross, R. Shaw, and R. W. Woolfolk, "Sensitivity Fundamentals," SRI Project 8525, Technical Progress Report 71-1 (Semiannual), April 9, 1971.
8. M. E. Hill, D. S. Ross, R. Shaw, R. W. Woolfolk, T. Mill, and L. B. Seely, "Sensitivity Fundamentals," SRI Project 4051, Final Report, May 1970.
9. D. J. Matthews, "Tables of the Velocity of Sound in Pure Water and Sea Water," Hydrographic Department, Admiralty, London, England, 1939.
10. N. E. Dorsey, "Properties of Ordinary Water-Substance," Reinhold, New York, 1940.
11. Stanford Research Institute Project 8525, Technical Progress Report, 70-1 (semiannual), "Sensitivity Fundamentals," October 2, 1970.
12. E. L. Lee, R. H. Sanborn, and H. D. Stromberg, Fifth Detonation Symposium, Pasadena, California, 1970, p. 271.

13. J. Zinn and C. L. Mader, J. Appl. Phys. 31, 323 (1960).
14. Yu. Ya. Maksimov, Russ. J. Phys. Chem. 5, 635 (1967).
15. R. N. Rogers, Thermochim. Acta 00, 000 (1972).
16. I. B. Rabinovich and V. A. Gorbushenkov, Dokl. Akad. Nauk SSSR 120, 566 (1958).
17. G. M. Nazin, G. B. Manelis, and F. I. Dubovitskii, Bull. Acad. Sci. USSR, Div. of Chem. Sci, 374 (1965).